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<p>(54) Title: MIXED OLEFIN POLYMERIZATION CATALYSTS, PROCESSES EMPLOYING SUCH CATALYSTS, AND POLYMERS OBTAINED THEREFROM</p> <p>(57) Abstract</p> <p>Mixed olefin polymerization catalysts, methods for preparing olefin polymers using the catalysts, and polymers obtained therefrom are disclosed. The mixed catalyst system comprises the combination of (a) a Group 8-10 transition metal complex of a first compound selected from Set 1, (b) either a Group 8-10 transition metal complex of a second compound selected from Set 1 or Set 2, or a Group 4 transition metal complex of Set 3 or Set 4, and optionally (c) a compound Y.</p>			

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**MIXED OLEFIN POLYMERIZATION CATALYSTS,
PROCESSES EMPLOYING SUCH CATALYSTS,
AND POLYMERS OBTAINED THEREFROM**

5

FIELD OF THE INVENTION

The present invention generally relates to mixed olefin polymerization catalysts, processes employing such catalysts, and polymers obtained therefrom. The novel catalysts comprise the combination of (a) a Group 8-10 transition metal complex of a first compound selected from Set 1, (b) 10 either a Group 8-10 transition metal complex of a second compound selected from Set 1 or Set 2, or a Group 4-6 transition metal complex of Set 3 or Set 4, and optionally (c) a compound Y.

BACKGROUND OF THE INVENTION

15 Olefin polymers are used in a wide variety of products, from sheathing for wire and cable to film. Olefin polymers are used, for instance, in injection or compression molding applications, in extruded films or sheeting, as extrusion coatings on paper, for example, photographic paper and digital recording paper, and the like. Improvements in catalysts have made it 20 possible to better control polymerization processes and, thus, influence the properties of the bulk material. Increasingly, efforts are being made to tune the physical properties of plastics for lightness, strength, resistance to corrosion, permeability, optical properties, and the like for particular uses. Chain length, polymer branching, and functionality have a significant impact 25 on the physical properties of the polymer. Accordingly, novel catalysts are

constantly being sought in attempts to obtain a catalytic process for polymerizing olefins which permits more efficient and better-controlled polymerization of olefins.

Conventional polyolefins are prepared by a variety of polymerization

5 techniques, including homogeneous liquid phase, gas phase, and slurry polymerization. Certain transition metal catalysts, such as those based on titanium compounds (e.g., $TiCl_3$ or $TiCl_4$) in combination with organoaluminum cocatalysts, are used to make linear and linear low-density polyethylenes as well as poly- α -olefins such as polypropylene. These so-

10 called "Ziegler-Natta" catalysts are quite sensitive to oxygen and are ineffective for the copolymerization of nonpolar and polar monomers.

Recent advances in non-Ziegler-Natta olefin polymerization catalysis include the following:

L.K. Johnson et al., WO 96/23010, disclose the polymerization of

15 olefins using cationic nickel, palladium, iron, and cobalt complexes containing diimine and bisoxazoline ligands. This document also describes the polymerization of ethylene, acyclic olefins, and/or selected cyclic olefins and optionally selected unsaturated acids or esters such as acrylic acid or alkyl acrylates to provide olefin homopolymers or copolymers.

20 European Patent Application No. 381,495 describes the polymerization of olefins using palladium and nickel catalysts that contain selected bidentate phosphorous containing ligands.

L.K. Johnson et al., *J. Am. Chem. Soc.*, 1995, 117, 6414, describe the polymerization of olefins such as ethylene, propylene, and 1-hexene using cationic α -diimine-based nickel and palladium complexes. These catalysts are said to polymerize ethylene to high molecular weight branched

5 polyethylene. In addition to ethylene, Pd complexes act as catalysts for the polymerization and copolymerization of olefins and methyl acrylate.

Eastman Chemical Company has recently described in a series of patent applications (WO 98/40374, WO 98/37110, WO 98/47933, and WO 98/40420) several new classes of Group 8-10 transition metal catalysts for

10 the polymerization of olefins. Also described are several new polymer compositions derived from epoxybutene and derivatives thereof.

G.F. Schmidt et al., *J. Am. Chem. Soc.*, 1985, 107, 1443, describe a cobalt(III) cyclopentadienyl catalytic system having the structure $[C_5Me_5(L)CoCH_2CH_2-\mu-H]^+$, which provides for the "living" polymerization of

15 ethylene.

M. Brookhart et al., *Macromolecules*, 1995, 28, 5378, disclose using such "living" catalysts in the synthesis of end-functionalized polyethylene homopolymers.

U. Klabunde, U.S. Patent Nos. 4,906,754, 4,716,205, 5,030,606, and

20 5,175,326, describes the conversion of ethylene to polyethylene using anionic phosphorous, oxygen donors ligated to Ni(II). The polymerization reactions were run between 25 and 100°C with modest yields, producing linear polyethylene having a weight-average molecular weight ranging

between 8K and 350K. In addition, Klabunde describes the preparation of copolymers of ethylene and functional group containing monomers.

M. Peuckert et al., *Organomet.*, 1983, 2(5), 594, disclose the oligomerization of ethylene using phosphine/carboxylate donors ligated to

5 Ni(II), which showed modest catalytic activity (0.14 to 1.83 TO/s). The oligomerizations were carried out at 60 to 95°C and 10 to 80 bar ethylene in toluene to produce α -olefins.

R.E. Murray, U.S. Patent Nos. 4,689,437 and 4,716,138, describes the oligomerization of ethylene using phosphine/sulfonate donors ligated to

10 Ni(II). These complexes show catalyst activities approximately 15 times greater than those reported with phosphine/carboxylate analogs.

W. Keim et al., *Angew. Chem. Int. Ed. Eng.*, 1981, 20, 116, and V.M. Mohring et al., *Angew. Chem. Int. Ed. Eng.*, 1985, 24, 1001, disclose the polymerization of ethylene and the oligomerization of α -olefins with

15 aminobis(imino)phosphorane nickel catalysts.

G. Wilke, *Angew. Chem. Int. Ed. Eng.*, 1988, 27, 185, describes a nickel allyl phosphine complex for the polymerization of ethylene.

K.A.O. Starzewski et al., *Angew. Chem. Int. Ed. Engl.* 1987, 26, 63, and U.S. Patent No. 4,691,036, describe a series of bis(ylide) nickel

20 complexes, used to polymerize ethylene to provide high molecular weight linear polyethylene.

WO 97/02298 discloses the polymerization of olefins using a variety of neutral N, O, P, or S donor ligands, in combination with a nickel(0) compound and an acid.

Brown et al., WO 97/17380, describe the use of Pd α -diimine

5 catalysts for the polymerization of olefins including ethylene in the presence of air and moisture.

Fink et al., U.S. Patent No. 4,724,273, describe the polymerization of α -olefins using aminobis(imino)phosphorane nickel catalysts and the compositions of the resulting poly(α -olefins).

10 Recently, Vaughan et al., WO 97/48736, Denton et al., WO 97/48742, and Sugimura et al., WO 97/38024, describe the polymerization of ethylene using silica supported α -diimine nickel catalysts.

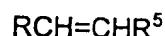
Also recently, Canich et al., WO 97/48735, and Mecking, DE 19707236 A1, describe the use of mixed α -diimine catalysts with group IV transition metal catalysts for the polymerization of olefins. Additional recent developments are described by Sugimura et al. in JP 96-84344 and JP 96-84343, by Yorisue et al. in JP 96-70332, by McLain et al. in WO 98/03559, by Weinberg et al. in WO 9803521, and by Matsunaga et al. in WO 97/48737.

20 Notwithstanding these advances in non-Ziegler-Natta catalysis, there remains a need for efficient and effective Group 8-10 transition metal catalysts for effecting polymerization of olefins. In addition, there is a need for novel methods of polymerizing olefins employing such effective Group 8-

10 transition metal catalysts. In particular, there remains a need for Group 8-10 transition metal olefin polymerization catalysts with both improved temperature stability and functional group compatibility. Further, there remains a need for a method of polymerizing olefins utilizing effective Group 5 8-10 transition metal catalysts in combination with a Lewis acid so as to obtain a catalyst that is more active and more selective.

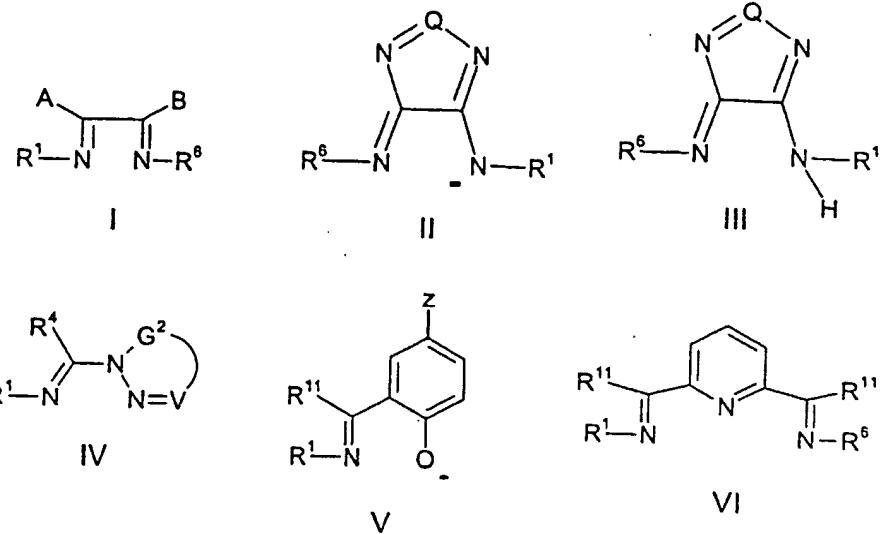
SUMMARY OF THE INVENTION

The present invention relates to a process for the polymerization of 10 olefins, which comprises contacting one or more olefin monomers of the formula Li :

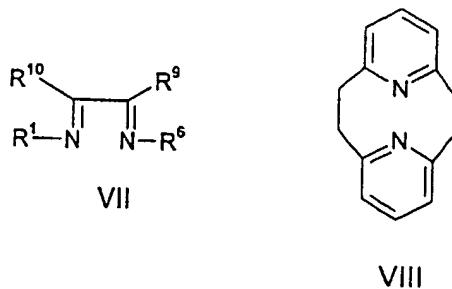


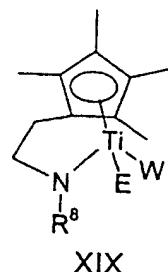
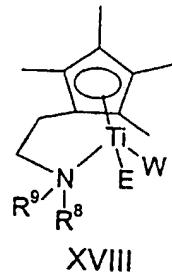
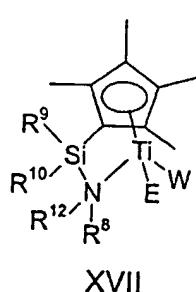
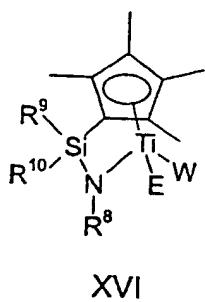
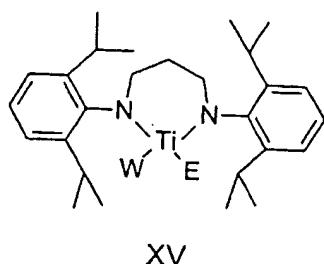
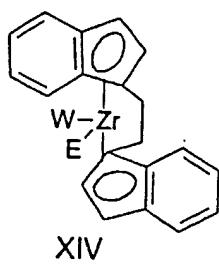
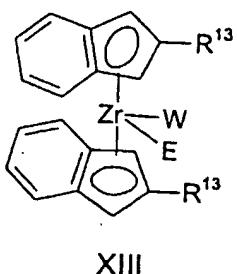
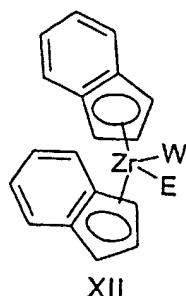
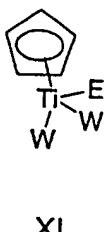
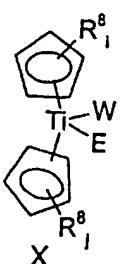
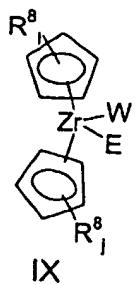
Li

with a mixed catalyst system comprising (a) a Group 8-10 transition metal 15 complex of a first compound selected from Set 1, (b) either a Group 8-10 transition metal complex of a second compound selected from Set 1 or Set 2, or a Group 4-6 transition metal complex of Set 3 or Set 4, and optionally (c) a compound Y ,

Set 1

5

Set 2

Set 3Set 4

TiCl_n/MgCl₂ or Silica/R₇Al

XX

Silica Supported Chromium Catalyst

XXI

wherein R and R⁵ each independently represent a hydrogen atom, a hydrocarbyl or a fluoroalkyl, and may be linked to form a cyclic olefin;

R¹ and R⁶ are each independently hydrocarbyl, substituted hydrocarbyl, or silyl;

5 R⁷ is hydrocarbyl;

R⁸, R⁹, and R¹⁰ are each independently a hydrogen atom, hydrocarbyl, or substituted hydrocarbyl; wherein i and j are each independently a whole number from 1 to 5;

R¹¹ is a hydrogen atom, hydrocarbyl, substituted hydrocarbyl,

10 heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl, or silyl;

R¹² and R¹³ are each independently hydrocarbyl or substituted hydrocarbyl;

E and W are each independently hydrocarbyl, chloride, bromide or
15 iodide;

Z is a hydrogen atom, hydrocarbyl, substituted hydrocarbyl, OR⁸, NO₂, or CF₃;

n is 3 or 4;

A and B are each independently a heteroatom connected mono-
20 radical wherein the connected heteroatom is selected from Group 15 or 16, and wherein A and B may be linked by a bridging group;

Q is C-R⁴, where R⁴ is hydrocarbyl, substituted hydrocarbyl, heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl, or O-Si(tert-butyl)(CH₃)₂;

G² is hydrocarbyl or substituted hydrocarbyl and may comprise a

5 carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G², V, N, and N;

V is CR¹⁴, N, or PR¹⁴R¹⁵; wherein R¹⁴ and R¹⁵ are each independently selected from H, hydrocarbyl, substituted hydrocarbyl, silyl and heteroatom connected hydrocarbyl, and wherein R¹⁴ and R¹⁵ may collectively form a ring

10 with phosphorus; and

Y is selected from the group consisting of a neutral Lewis acid capable of abstracting E⁻ or W⁻ to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, and a Bronsted acid whose conjugate base is a weakly coordinating anion,

15 provided that when a compound of **Set 3** is part of the mixed catalyst system, a compound Y is present, and

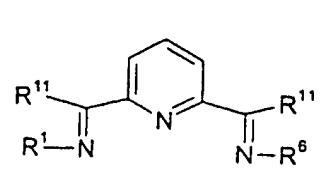
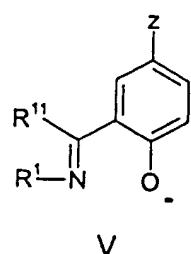
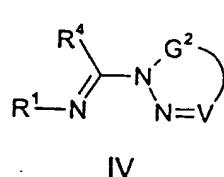
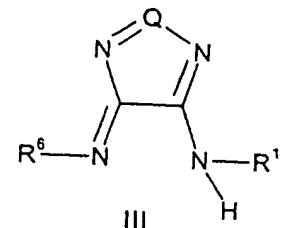
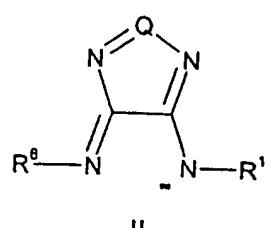
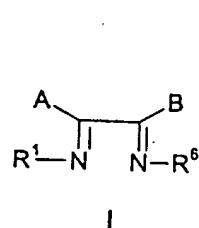
provided that when a compound of the formula VI is used, the Group 8-10 transition metal is Fe or Co.

The present invention further relates to new polyolefins that are made
20 by the novel mixed catalyst system described herein. The polyolefins preferably contain long chain branching at greater than 0.1 long chain branches per polymer chain.

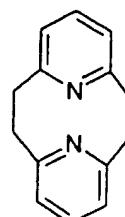
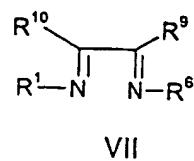
The present invention further relates to a mixed catalyst composition, which comprises (a) a Group 8-10 transition metal complex of a first compound selected from **Set 1**, (b) either a Group 8-10 transition metal complex of a second compound selected from **Set 1** or **Set 2**, or a Group 4-6 transition metal complex of **Set 3** or **Set 4**, and optionally (c) a compound Y,

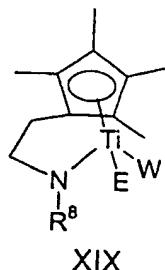
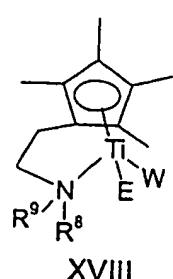
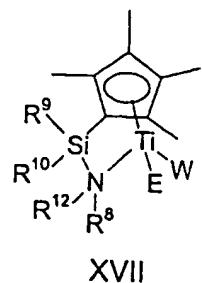
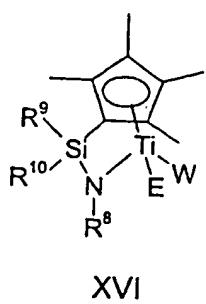
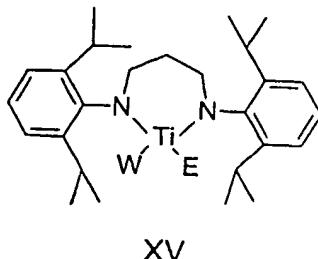
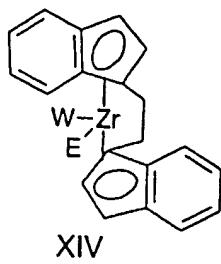
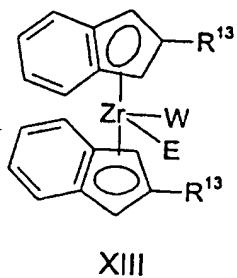
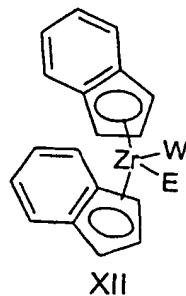
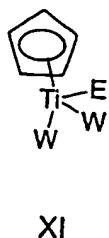
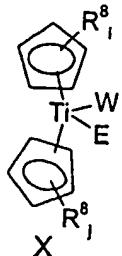
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Set 1



10 Set 2



Set 3Set 4

TiCl_n/MgCl₂ or Silica/R₇Al

Silica Supported Chromium Catalyst

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wherein R and R⁵ each independently represent a hydrogen atom, a hydrocarbyl or a fluoroalkyl, and may be linked to form a cyclic olefin;

R¹ and R⁶ are each independently hydrocarbyl, substituted hydrocarbyl, or silyl;

5 R⁷ is hydrocarbyl;

R⁸, R⁹, and R¹⁰ are each independently a hydrogen atom, hydrocarbyl, or substituted hydrocarbyl; wherein i and j are each independently a whole number from 1 to 5;

R¹¹ is a hydrogen atom, hydrocarbyl, substituted hydrocarbyl,

10 heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl, or silyl;

R¹² and R¹³ are each independently hydrocarbyl or substituted hydrocarbyl;

E and W are each independently hydrocarbyl, chloride, bromide or

15 iodide;

Z is a hydrogen atom, hydrocarbyl, substituted hydrocarbyl, OR⁸, NO₂, or CF₃;

n is 3 or 4;

A and B are each independently a heteroatom connected mono-

20 radical wherein the connected heteroatom is selected from Group 15 or 16, and wherein A and B may be linked by a bridging group;

Q is C-R⁴, where R⁴ is hydrocarbyl, substituted hydrocarbyl, heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl, or O-Si(tert-butyl)(CH₃)₂;

G² is hydrocarbyl or substituted hydrocarbyl and may comprise a 5

5 carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G², V, N, and N;

V is CR¹⁴, N, or PR¹⁴R¹⁵, wherein R¹⁴ and R¹⁵ are each independently selected from H, hydrocarbyl, substituted hydrocarbyl, silyl and heteroatom connected hydrocarbyl, and wherein R¹⁴ and R¹⁵ may collectively form a ring 10 with phosphorus; and

Y is selected from the group consisting of a neutral Lewis acid capable of abstracting E⁻ or W⁻ to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, and a Bronsted acid whose conjugate base is a weakly coordinating anion, 15 provided that when a compound of **Set 3** is part of the mixed catalyst system, a compound Y is present, and

provided that when a compound of the formula VI is used, the Group 8-10 transition metal is Fe or Co.

DETAILED DESCRIPTION OF THE INVENTION

In this disclosure, certain chemical groups or compounds are described by certain terms and symbols. The terms and symbols are defined below.

5 Symbols ordinarily used to denote elements in the Periodic Table take their ordinary meaning, unless otherwise specified. Thus, N, O, S, P, and Si stand for nitrogen, oxygen, sulfur, phosphorus, and silicon, respectively.

10 Examples of neutral Lewis acids include, but are not limited to, methylaluminoxane (hereinafter "MAO") and other aluminum sesquioxides, R^{16}_3Al , R^{16}_2AlCl , $R^{16}AlCl_2$ (where R^{16} is alkyl), organoboron compounds, boron halides, $B(C_6F_5)_3$, BPh_3 , and $B(3,5-(CF_3)C_6H_3)_3$.

15 Examples of ionic compounds comprising a cationic Lewis acid include: $R^{17}_3Sn[BF_4]$ (where R^{17} is hydrocarbyl), $MgCl_2$, and H^+X^- (where X^- is a weakly coordinating anion).

20 The term "weakly coordinating anion" is well-known in the art *per se* and generally refers to a large bulky anion capable of delocalization of the negative charge of the anion. Suitable weakly coordinating anions include, but are not limited to, PF_6^- , BF_4^- , SbF_6^- , $(Ph)_4B^-$ wherein Ph = phenyl, and tBAr_4 wherein tBAr_4 = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate. The coordinating ability of such anions is known and described in the literature. See, e.g., S. Strauss et al., *Chem. Rev.*, 1993, 93, 927.

Examples of neutral Lewis bases include, but are not limited to, (i) ethers, for example, diethyl ether and tetrahydrofuran; (ii) organic nitriles, for

example, acetonitrile; (iii) organic sulfides, for example, dimethylsulfide; and (iv) monoolefins, for example, ethylene, hexene and cyclopentene.

A "hydrocarbyl" group means a monovalent or divalent, linear, branched or cyclic group that contains only carbon and hydrogen atoms.

- 5 Examples of monovalent hydrocarbyls include the following: C₁-C₂₀ alkyl; C₁-C₂₀ alkyl substituted with one or more groups selected from C₁-C₂₀ alkyl, C₃-C₈ cycloalkyl, and aryl; C₃-C₈ cycloalkyl; C₃-C₈ cycloalkyl substituted with one or more groups selected from C₁-C₂₀ alkyl, C₃-C₈ cycloalkyl, and aryl; C₆-C₁₄ aryl; and C₆-C₁₄ aryl substituted with one or more groups selected
- 10 from C₁-C₂₀ alkyl, C₃-C₈ cycloalkyl, and aryl, where the term "aryl" preferably denotes a phenyl, napthyl, or anthracenyl group. Examples of divalent (bridging) hydrocarbyls include: -CH₂-, -CH₂CH₂-, -CH₂CH₂CH₂-, and 1,2-phenylene.

A "silyl" group refers to a SiR₃ group wherein Si is silicon and R is

- 15 hydrocarbyl or substituted hydrocarbyl or silyl, as in Si(SiR₃)₃.

A "heteroatom" refers to an atom other than carbon or hydrogen. Preferred heteroatoms include oxygen, nitrogen, phosphorus, sulfur, selenium, arsenic, chlorine, bromine, silicon, and fluorine.

A "substituted hydrocarbyl" refers to a monovalent or divalent

- 20 hydrocarbyl substituted with one or more heteroatoms. Examples of monovalent substituted hydrocarbyls include: 2,6-dimethyl-4-methoxyphenyl, 2,6-diisopropyl-4-methoxyphenyl, 4-cyano-2,6-dimethylphenyl, 2,6-dimethyl-4-nitrophenyl, 2,6-difluorophenyl, 2,6-

dibromophenyl, 2,6-dichlorophenyl, 4-methoxycarbonyl-2,6-dimethylphenyl, 2-tert-butyl-6-chlorophenyl, 2,6-dimethyl-4-phenylsulfonylphenyl, 2,6-dimethyl-4-trifluoromethylphenyl, 2,6-dimethyl-4-trimethylammoniumphenyl (associated with a weakly coordinated anion), 2,6-dimethyl-4-hydroxyphenyl,

5 9-hydroxyanthr-10-yl, 2-chloronaph-1-yl, 4-methoxyphenyl, 4-nitrophenyl, 9-nitroanthr-10-yl, -CH₂OCH₃, cyano, trifluoromethyl, and fluoroalkyl.

Examples of divalent (bridging) substituted hydrocarbyls include: 4-methoxy-1,2-phenylene, 1-methoxymethyl-1,2-ethanediyl, 1,2-bis(benzyloxymethyl)-1,2-ethanediyl, and 1-(4-methoxyphenyl)-1,2-ethanediyl.

10

10 ethanediyl.

A "heteroatom connected mono-radical" refers to a mono-radical group in which a heteroatom serves as the point of attachment.

Examples include: NH(2,6-dimethylphenyl) and SPh, where Ph is phenyl.

Numerous other examples are given herein.

15 A "substituted silicon atom" refers to a -SiR¹⁸₂- group, wherein R¹⁸ is a hydrocarbyl or substituted hydrocarbyl.

A "substituted phosphorous atom" refers to a -P(O)(OR¹⁸)- group, wherein R¹⁸ is a hydrocarbyl or substituted hydrocarbyl.

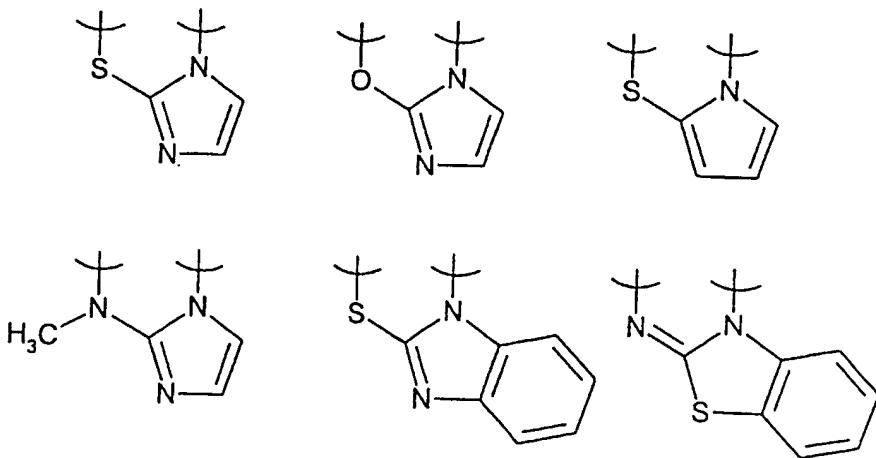
20 A "substituted sulfur atom" refers to a -S(O)-, -SO₂-, or -S(NR¹⁸)₂- group, wherein R¹⁸ is a hydrocarbyl or substituted hydrocarbyl.

A "bridging group" refers to a divalent hydrocarbyl, divalent substituted hydrocarbyl, -C(O)-, -C(S)-, substituted silicon atom, substituted

sulfur atom, substituted phosphorous atom, -CH₂C(O)-, -C(O)C(O)-, or 3,4,5,6-tetrafluoro-1,2-phenylene.

In certain cases, the bridging group, together with groups A and B, may collectively form a divalent heteroatom substituted heterocycle.

5 Examples of such heterocycles include:



A "mono-olefin" refers to a hydrocarbon containing one carbon-carbon double bond.

10 double bond.

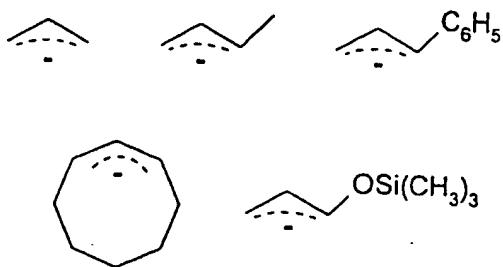
The term "fluoroalkyl" as used herein refers to a C₁-C₂₀ alkyl group substituted by one or more fluorine atoms.

The term "polymer" as used herein refers to a species comprised of monomer units and having a degree of polymerization (DP) of ten or higher.

15 The term "α-olefin" as used herein is a 1-alkene with from 3 to 40 carbon atoms.

A "π-allyl" group refers to a monoanionic group with three sp^2 carbon atoms bound to a metal center in a η^3 -fashion. Any of the three sp^2 carbon atoms may be substituted with a hydrocarbyl, substituted hydrocarbyl, heteroatom connected hydrocarbyl, heteroatom connected substituted

5 hydrocarbyl, or O-silyl group. Examples of π -allyl groups include:



The term π -benzyl group denotes an π -allyl group where two of the sp^2 carbon atoms are part of an aromatic ring. Examples of π -benzyl groups

10 include:



As used herein, the term "long chain branching" refers to a branch approaching the length of a polymer chain (e.g., >100 carbons).

As used herein, the terms "monomer" and "olefin monomer" refer to the olefin or other monomer compound before it has been polymerized; the term "monomer units" refers to the moieties of a polymer that correspond to the monomers after they have been polymerized.

- 5 In some cases, a compound Y is required as a cocatalyst. Suitable compounds Y include a neutral Lewis acid capable of abstracting E⁻ or W⁻ to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, and a Bronsted acid whose conjugate base is a weakly coordinating anion. Preferred compounds Y include:
- 10 methylaluminoxane (hereinafter "MAO") and other aluminum sesquioxides, R¹⁶₃Al, R¹⁶₂AlCl, R¹⁶AlCl₂ (wherein R¹⁶ is alkyl), organoboron compounds, boron halides, B(C₆F₅)₃, R¹⁷₃Sn[BF₄] (wherein R¹⁷ hydrocarbyl), MgCl₂, and H⁺X⁻ (wherein X⁻ is a weakly coordinating anion). Examples of H⁺X⁻ include the ether solvate of hydrogen tetrakis[3,5-bis(trifluoromethyl)phenyl]borate
- 15 and montmorillonite clay.

The relative amounts of catalyst components (a), (b), and (c) used in the mixed catalyst system of the present invention can vary over a wide range. The precise amount of each component employed depends on the desired properties and characteristics of the resulting polymer. Generally,

- 20 the mixed catalyst system may contain from about 1 to about 99% by weight of component (a), from about 1 to about 99% by weight of component (b), and from about 10 to 10,000 molar equivalents of component (c) based on the amount of components (a) and (b).

Also described herein is a process for the polymerization of olefins.

Preferred olefins include ethylene and α -olefins such as propylene, 1-butene, 1-hexene, 1-octene, and cyclic olefins such as cyclopentene.

The polymerization processes described herein may be carried out in

- 5 a batch or continuous mode of operation. The processes may be conducted as solution polymerizations, as non-solvent slurry type polymerizations, as slurry polymerizations using one or more of the olefins or other solvent as the polymerization medium, or in the gas phase. The catalyst employed may be unsupported or supported using a suitable catalyst support and methods
- 10 known in the art. When the catalyst is in supported form, the supported catalyst may be used in slurry or gas phase polymerizations.

Examples of "solid support" include inorganic oxide support materials, such as: talcs, silicas, titania, silica/chromia, silica/chromia/titania, silica/alumina, zirconia, aluminum phosphate gels, silanized silica, silica

- 15 hydrogels, silica xerogels, silica aerogels, montmorillonite clay and silica co-gels as well as organic solid supports such as polystyrene and functionalized polystyrene. See, for example, S.B. Roscoe et al., "Polyolefin Spheres from Metallocenes Supported on Non-Interacting Polystyrene", *Science*, 1998, 280, 270-273.

- 20 An especially preferred solid support is one which has been pre-treated with compound(s) Y as described herein, most preferably with MAO. Thus, in a preferred embodiment, the catalysts of the present invention are attached to a solid support (by "attached to a solid support" is meant ion

paired with a component on the surface, adsorbed to the surface or covalently attached to the surface) which has been pre-treated with a compound Y. Alternatively, the catalyst, the compound Y, and the solid support can be combined in any order, and any number of compounds Y can

5 be utilized. In addition, the supported catalyst thus formed, may be treated with additional quantities of compound(s) Y. In an especially preferred embodiment, the catalyst components of the present invention are attached to silica which has been pre-treated with MAO. Such supported catalysts are prepared by contacting the transition metal compound, in a substantially

10 inert solvent -- by which is meant a solvent which is either unreactive under the conditions of catalyst preparation, or if reactive, acts to usefully modify the catalyst activity or selectivity -- with MAO treated silica for a sufficient period of time to generate the supported catalysts. Examples of substantially inert solvents include toluene, mineral spirits, hexane, CH_2Cl_2

15 and CHCl_3 .

Polymerization temperature and pressure have significant effects on (co)polymer structure, composition, and molecular weight. Suitable (co)polymerization temperatures preferably range from about -100°C to about 200°C, more preferably from 20°C to 150°C. Suitable

20 (co)polymerization pressures preferably range from 1 atmosphere to 1000 atmospheres, and more preferably from 1 to 100 atmospheres.

After the reaction has proceeded for a time sufficient to produce the desired polymers, the polymer can be recovered from the reaction mixture by routine methods of isolation and/or purification.

High molecular weight resins are readily processed using

- 5 conventional extrusion, injection molding, compression molding, and vacuum forming techniques well known in the art. Useful articles made from them include films, fibers, bottles and other containers, sheeting, molded objects and the like.

Low molecular weight resins are useful, for example, as synthetic

- 10 waxes and they may be used in various wax coatings or in emulsion form. They are also particularly useful in blends with ethylene/vinyl acetate or ethylene/methyl acrylate-type copolymers in paper coating or in adhesive applications.

Although not required, typical additives used in olefin or vinyl

- 15 polymers may be used in the new homopolymers and copolymers of this invention. Typical additives include pigments, colorants, titanium dioxide, carbon black, antioxidants, stabilizers, slip agents, flame retarding agents, and the like. These additives and their use in polymer systems are known *per se* in the art.
- 20 Other features of the invention will become apparent in the following description of working examples, which have been provided for illustration of the invention and are not intended to be limiting thereof.

EXAMPLES**Example 1**

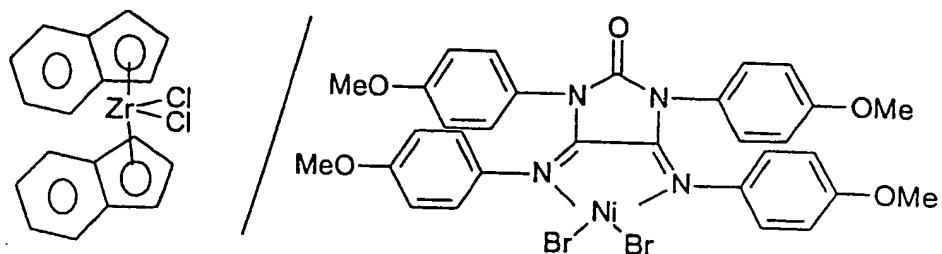
Ethylene polymerization using the mixed catalyst system bis(indenyl)zirconium dimethyl and the nickel complex of 2,3-bis(2,6-

5 dimethylphenylimino)-[1,4]dithiane.

A flame dried, pear-shaped flask equipped with a stir bar and a septum was charged with 0.4 mg (1.1 μ mol) of bis(indenyl)zirconium dimethyl and 0.5 mg (0.87 μ mol) of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane. The solid mixture was removed
10 from the inert atmosphere glove box, and 50 mL of toluene and 3.0 mL of modified-MAO (Akzo Nobel) were added. The reaction was rapidly stirred at 23°C and 1 atm ethylene for 1 minute. After 1 minute, a significant amount of polymer had precipitated, and the reaction was quenched upon addition of MeOH, acetone, and 6 M HCl. The polymer (0.5 g) was collected by suction
15 filtration, washed with acetone and dried *in vacuo* for several hours. DSC: (2nd heat) melt with an endothermic maximum at 137°C. 1 H NMR: 5 branches/1000 carbon atoms.

Example 2

Preparation of LLDPE from a mixed early/late transition metal catalyst system.



5

A flame dried, pear-shaped flask equipped with a stir bar and a septum was charged with 2 mg (0.87 μ mol) of the nickel dibromide complex shown above. The flask was removed from the inert atmosphere glove box, and 50 mL of toluene and 3.0 mL of modified-MAO (Akzo Nobel) were added. The reaction was rapidly stirred at 25°C and 1 atm ethylene for 15 minutes. The nickel catalyst rapidly oligomerized ethylene as indicated by the ethylene uptake in the system. After 15 minutes, 0.4 mg (1.1 μ mol) of bis(indenyl)zirconium dimethyl catalyst was added, a significant amount of polymer began to precipitate, and the reaction was quenched upon addition of MeOH, acetone, and 6 M HCl after an additional 10 minutes. The polymer (0.3 g) was collected by suction filtration, washed with acetone and dried *in vacuo* for several hours. DSC: (2nd heat) melt with an endothermic

maximum at 128°C. ^1H NMR: 5 branches/1000 carbon atoms. GPC: Mn = 57,000; Mw/Mn = 1.89.

Example 3

5 Synthesis of the supported mixed catalyst nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane/bis(indenyl)zirconium dimethyl.

A flame dried, pear-shaped flask equipped with a stir bar and a septum was charged with 10 mg (17 μmol) of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane, 3 mg of

10 bis(indenyl)zirconium dimethyl and 1 g of MAO treated silica (purchased from Witco TA 02794/HL/04). The solid mixture was cooled to 0°C in an ice bath, and 20 mL of CH_2Cl_2 was added. The reaction was rapidly stirred at 0°C for 1 hour. After 1 hour, the solid was allowed to settle, and the solvent was removed *in vacuo*. The resulting brown solid was dried under dynamic

15 vacuum giving 983 mg of supported catalyst material.

Example 4

Polymerization of ethylene using the mixed catalyst prepared in Example 3.

20 A 600 mL Parr® autoclave was first heated to about 100°C under dynamic vacuum to ensure the reactor was dry. The reactor was then purged with argon. The 600 mL Parr® autoclave was charged in the inert atmosphere glove box with 300 g of dried NaCl and 100 mg of the mixed

supported catalyst prepared in Example 3. Upon removing the autoclave from the glove box, the reactor was rapidly pressurized to 200 psig ethylene. After 30 minutes at 80°C, the reaction was quenched and the polyethylene isolated by blending the polyethylene/salt mixture in warm water and

- 5 collecting the resulting polymer by filtration. The polyethylene was dried for several hours in a vacuum oven at 100°C resulting in 13.5 g of a white polyethylene. ^1H NMR: 10 branches/1000 carbon atoms. GPC: Mn = 47,800; Mw/Mn = 3.99.

10

Example 5

Polymerization of ethylene using the mixed catalyst prepared in Example 3.

A 600 mL Parr® autoclave was first heated to about 100°C under dynamic vacuum to ensure the reactor was dry. The reactor was then

- 15 purged with argon. The 600 mL Parr® autoclave was charged in the inert atmosphere glove box with 300 g of dried NaCl and 50 mg of the mixed supported catalyst prepared in Example 3. Upon removing the autoclave from the box, the reactor was rapidly pressurized to 200 psig ethylene. After 15 minutes at 80°C, the reaction was quenched and the polyethylene
- 20 isolated by blending the polyethylene/salt mixture in warm water and collecting the resulting polymer by filtration. The polyethylene was dried for several hours in a vacuum oven at 100°C resulting in 1.5 g of a white

polyethylene. ^1H NMR: 24 branches/1000 carbon atoms. GPC: Mn = 47,300; Mw/Mn = 4.57.

Example 6

5 Polymerization of ethylene using the mixed catalyst prepared in Example 3.

A 600 mL Parr® autoclave was first heated to about 100°C under dynamic vacuum to ensure the reactor was dry. The reactor was then purged with argon. The 600 mL Parr® autoclave was charged in the inert

10 atmosphere glove box with 300 g of dried NaCl and 50 mg of the mixed supported catalyst prepared in Example 3. Upon removing the autoclave from the glove box, the reactor was rapidly pressurized to 200 psig ethylene.

After 60 minutes at 80°C, the reaction was quenched and the polyethylene isolated by blending the polyethylene/salt mixture in warm water and

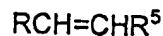
15 collecting the resulting polymer by filtration. The polyethylene was dried for several hours in a vacuum oven at 100°C resulting in 6.15 g of a white polyethylene. ^1H NMR: 10 branches/1000 carbon atoms. GPC: Mn = 43,600; Mw/Mn = 4.11.

While the invention has been described with reference to preferred
20 embodiments and working examples, it is to be understood that variations and modifications may be resorted to as will be apparent to those skilled in the art. Such variations and modifications are to be considered within the

purview and scope of the invention as defined by the claims appended hereto.

WE CLAIM:

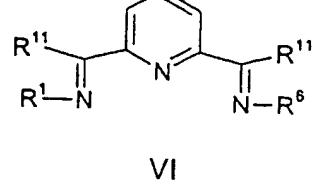
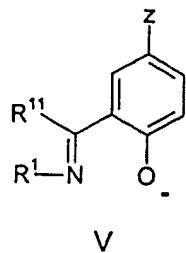
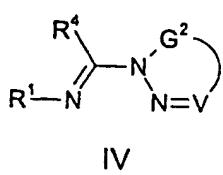
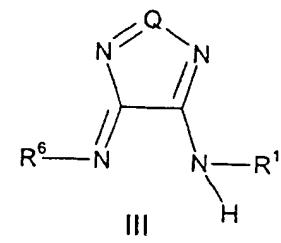
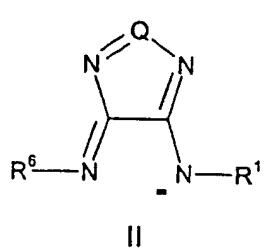
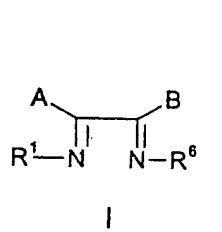
1. A process for the polymerization of olefins, which comprises contacting one or more olefin monomers of the formula LI:



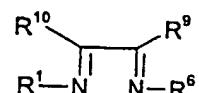
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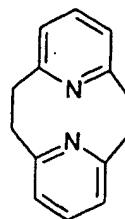
with a mixed catalyst system comprising (a) a Group 8-10 transition metal complex of a first compound selected from **Set 1**, (b) either a Group 8-10 transition metal complex of a second compound selected from **Set 1** or **Set 2**, or a Group 4-6 transition metal complex of **Set 3** or **Set 4**, and optionally 10 (c) a compound Y,

Set 1

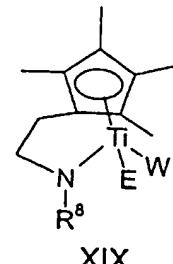
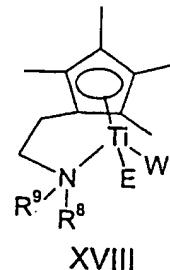
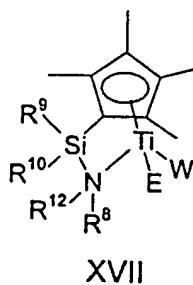
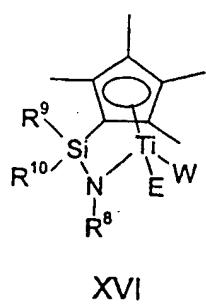
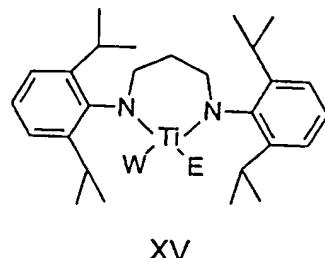
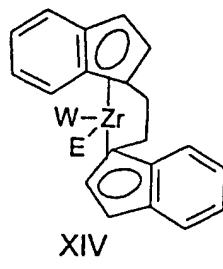
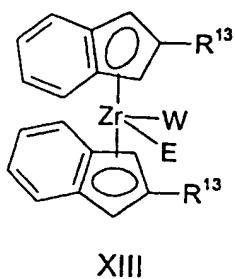
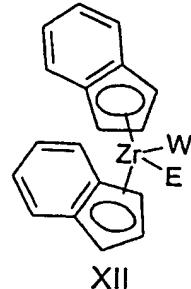
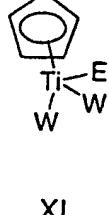
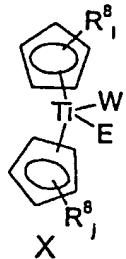
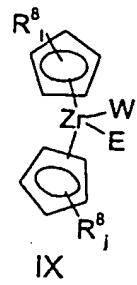
15

Set 2

VII



VIII

Set 3Set 4 $TiCl_n/MgCl_2$ or Silica/ R_3Al

Silica Supported Chromium Catalyst

XX

XXI

wherein R and R⁵ each independently represent a hydrogen atom, a hydrocarbyl or a fluoroalkyl, and may be linked to form a cyclic olefin;

R¹ and R⁶ are each independently hydrocarbyl, substituted hydrocarbyl, or silyl;

5 R⁷ is hydrocarbyl;

R⁸, R⁹, and R¹⁰ are each independently a hydrogen atom, hydrocarbyl, or substituted hydrocarbyl; wherein i and j are each independently a whole number from 1 to 5;

R¹¹ is a hydrogen atom, hydrocarbyl, substituted hydrocarbyl,

10 heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl, or silyl;

R¹² and R¹³ are each independently hydrocarbyl or substituted hydrocarbyl;

E and W are each independently hydrocarbyl, chloride, bromide or
15 iodide;

Z is a hydrogen atom, hydrocarbyl, substituted hydrocarbyl, OR⁸, NO₂, or CF₃;

n is 3 or 4;

A and B are each independently a heteroatom connected mono-
20 radical wherein the connected heteroatom is selected from Group 15 or 16,
and wherein A and B may be linked by a bridging group;

Q is C-R⁴, where R⁴ is hydrocarbyl, substituted hydrocarbyl, heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl, or O-Si(tert-butyl)(CH₃)₂;

G² is hydrocarbyl or substituted hydrocarbyl and may comprise a 5 carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G², V, N, and N;

V is CR¹⁴, N, or PR¹⁴R¹⁵; wherein R¹⁴ and R¹⁵ are each independently selected from H, hydrocarbyl, substituted hydrocarbyl, silyl and heteroatom connected hydrocarbyl, and wherein R¹⁴ and R¹⁵ may collectively form a ring with phosphorus; and

Y is selected from the group consisting of a neutral Lewis acid capable of abstracting E⁻ or W⁻ to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, and a Bronsted acid whose conjugate base is a weakly coordinating anion,

provided that when a compound of **Set 3** is part of the mixed catalyst system, a compound Y is present, and

provided that when a compound of the formula VI is used, the Group 8-10 transition metal is Fe or Co.

20 2. The process according to claim 1, wherein the mixed catalyst system comprises a Group 8-10 transition metal complex of a first compound selected from **Set 1** and a Group 8-10 transition metal complex of a second compound selected from **Set 1**.

3. The process according to claim 2, wherein the transition metal is nickel.

5 4. The process according to claim 2, wherein the mixed catalyst system comprises a nickel complex of compound I and an iron complex of compound VI.

10 5. The process according to claim 2, wherein the mixed catalyst system comprises a nickel complex of compound I and a cobalt complex of compound VI.

6. A polymer produced by the process according to claim 2.

15 7. The polymer according to claim 6, which contains long chain branching at greater than 0.1 long chain branches per polymer chain.

8. The process according to claim 1, wherein the mixed catalyst system comprises a Group 8-10 transition metal complex of a first compound 20 selected from Set 1 and a Group 8-10 transition metal complex of a second compound selected from Set 2.

9. The process according to claim 8, wherein the transition metal is nickel.
10. The process according to claim 8, wherein the mixed catalyst system comprises a nickel complex of compound I and a nickel complex of compound VII.
5
11. The process according to claim 8, wherein the mixed catalyst system comprises a nickel complex of compound I and a nickel complex of compound VIII.
10
12. A polymer produced by the process according to claim 8.
13. The polymer according to claim 12, which contains long chain branching at greater than 0.1 long chain branches per polymer chain.
15
14. The process according to claim 1, wherein the mixed catalyst system comprises a Group 8-10 transition metal complex of a first compound selected from **Set 1** and a Group 4 transition metal complex selected from
20 **Set 3**.
15. The process according to claim 14, wherein the Group 8-10 transition metal is nickel.

16. The process according to claim 14, wherein the mixed catalyst system comprises an iron complex of compound VI.

5 17. The process according to claim 14, wherein the mixed catalyst system comprises a cobalt complex of compound VI.

18. A polymer produced by the process according to claim 14.

10 19. The polymer according to claim 18, which contains long chain branching at greater than 0.1 long chain branches per polymer chain.

20. The process according to claim 1, wherein the mixed catalyst system comprises a Group 8-10 transition metal complex of a first compound selected from **Set 1** and a Group 4-6 transition metal complex selected from **Set 4**.

21. The process according to claim 20, wherein the Group 8-10 transition metal is nickel.

20

22. The process according to claim 20, wherein the mixed catalyst system comprises an iron complex of compound VI.

23. The process according to claim 20, wherein the mixed catalyst system comprises a cobalt complex of compound VI.

24. A polymer produced by the process according to claim 20.

5

25. The polymer according to claim 24, which contains long chain branching at greater than 0.1 long chain branches per polymer chain.

26. The process according to claim 2, wherein the mixed catalyst system is on a solid support.

10 27. The process according to claim 8, wherein the mixed catalyst system is on a solid support.

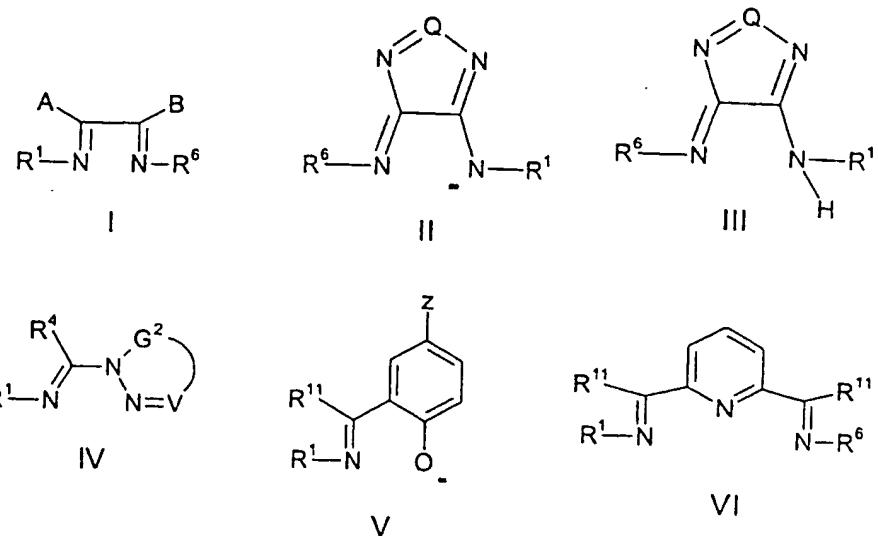
15 28. The process according to claim 14, wherein the mixed catalyst system is on a solid support.

20 29. The process according to claim 20, wherein the mixed catalyst system is on a solid support.

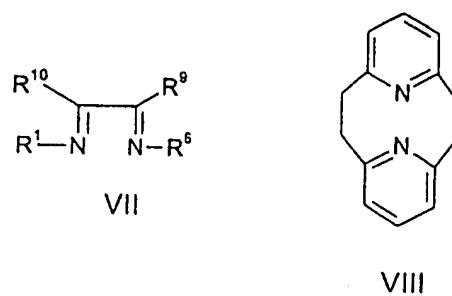
30. A mixed catalyst composition, which comprises (a) a Group 8-10 transition metal complex of a first compound selected from Set 1, (b) either a Group 8-10 transition metal complex of a second compound

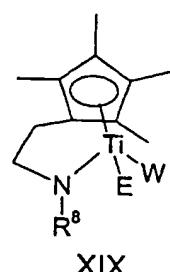
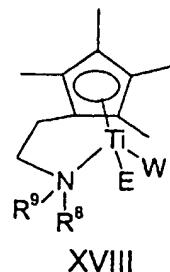
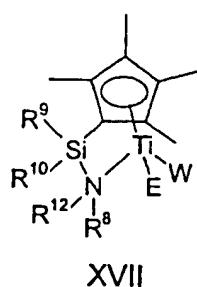
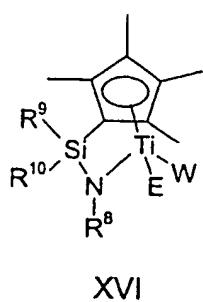
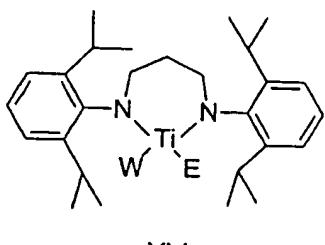
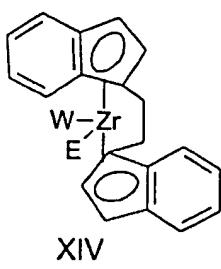
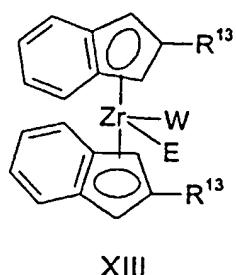
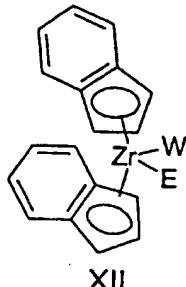
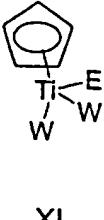
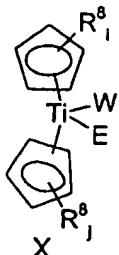
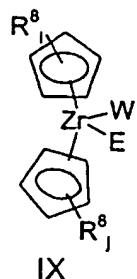
selected from Set 1 or Set 2, or a Group 4-6 transition metal complex of Set 3 or Set 4, and optionally (c) a compound Y,

5 Set 1



10 Set 2



Set 3Set 4 $TiCl_n/MgCl_2$ or Silica/R⁷Al

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Silica Supported Chromium Catalyst

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wherein R and R⁵ each independently represent a hydrogen atom, a hydrocarbyl or a fluoroalkyl, and may be linked to form a cyclic olefin;

R¹ and R⁶ are each independently hydrocarbyl, substituted hydrocarbyl, or silyl;

5 R⁷ is hydrocarbyl;

R⁸, R⁹, and R¹⁰ are each independently a hydrogen atom, hydrocarbyl, or substituted hydrocarbyl; wherein i and j are each independently a whole number from 1 to 5;

10 R¹¹ is a hydrogen atom, hydrocarbyl, substituted hydrocarbyl, heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl, or silyl;

R¹² and R¹³ are each independently hydrocarbyl or substituted hydrocarbyl;

15 E and W are each independently hydrocarbyl, chloride, bromide or iodide;

Z is a hydrogen atom, hydrocarbyl, substituted hydrocarbyl, OR⁸, NO₂, or CF₃;

n is 3 or 4;

20 A and B are each independently a heteroatom connected monoradical wherein the connected heteroatom is selected from Group 15 or 16, and wherein A and B may be linked by a bridging group;

Q is C-R⁴, where R⁴ is hydrocarbyl, substituted hydrocarbyl, heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl, or O-Si(tert-butyl)(CH₃)₂;

G² is hydrocarbyl or substituted hydrocarbyl and may comprise a

5 carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G², V, N, and N;

V is CR¹⁴, N, or PR¹⁴R¹⁵; wherein R¹⁴ and R¹⁵ are each independently selected from H, hydrocarbyl, substituted hydrocarbyl, silyl and heteroatom connected hydrocarbyl, and wherein R¹⁴ and R¹⁵ may collectively form a ring

10 with phosphorus; and

Y is selected from the group consisting of a neutral Lewis acid capable of abstracting E⁻ or W⁻ to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, and a Bronsted acid whose conjugate base is a weakly coordinating anion,

15 provided that when a compound of **Set 3** is part of the mixed catalyst system, a compound Y is present, and

provided that when a compound of the formula VI is used, the Group 8-10 transition metal is Fe or Co.

20 31. The catalyst composition according to claim 30, which comprises a Group 8-10 transition metal complex of a first compound selected from **Set 1** and a Group 8-10 transition metal complex of a second compound selected from **Set 1**.

32. The catalyst composition according to claim 31, wherein the transition metal is nickel.

5 33. The catalyst composition according to claim 31, which comprises a nickel complex of compound I and an iron complex of compound VI.

10 34. The catalyst composition according to claim 31, which comprises a nickel complex of compound I and a cobalt complex of compound VI.

15 35. The catalyst composition according to claim 30, which comprises a Group 8-10 transition metal complex of a first compound selected from **Set 1** and a Group 8-10 transition metal complex of a second compound selected from **Set 2**.

36. The catalyst composition according to claim 35, wherein the transition metal is nickel.

20

37. The catalyst composition according to claim 35, which comprises a nickel complex of compound I and a nickel complex of compound VII.

38. The catalyst composition according to claim 35, which comprises a nickel complex of compound I and a nickel complex of compound VIII.

5

39. The catalyst composition according to claim 30, which comprises a Group 8-10 transition metal complex of a first compound selected from Set 1 and a Group 4 transition metal complex selected from Set 3.

10

40. The catalyst composition according to claim 39, wherein the Group 8-10 transition metal is nickel.

41. The catalyst composition according to claim 39, which
15 comprises a cobalt complex of compound VI.

42. The catalyst composition according to claim 39, which comprises an iron complex of compound VI.

20

43. The catalyst composition according to claim 30, which comprises a Group 8-10 transition metal complex of a first compound selected from Set 1 and a Group 4-6 transition metal complex selected from Set 4.

44. The catalyst composition according to claim 43, wherein the group 8-10 transition metal is nickel.

45. The catalyst composition according to claim 43, which
5 comprises an iron complex of compound VI.

46. The catalyst composition according to claim 43, which
comprises a cobalt complex of compound VI.

10 47. The catalyst composition according to claim 31, which is on a
solid support.

48. The catalyst composition according to claim 35, which is on a
solid support.

15

49. The catalyst composition according to claim 39, which is on a
solid support.

50. The catalyst composition according to claim 43, which is on a
20 solid support.

51. The process according to claim 8, wherein the mixed catalyst system comprises an iron complex of compound VI and a nickel complex selected from **Set 2**.

5 52. The process according to claim 8, wherein the mixed catalyst system comprises a cobalt complex of compound VI and a nickel complex selected from **Set 2**.

10 53. The process according to claim 26, wherein the solid support is silica.

54. The process according to claim 27, wherein the solid support is silica.

15 55. The process according to claim 28, wherein the solid support is silica.

56. The process according to claim 29, wherein the solid support is silica.

20

57. The catalyst composition according to claim 47, wherein the solid support is silica.

58. The catalyst composition according to claim 48, wherein the solid support is silica.

59. The catalyst composition according to claim 49, wherein the 5 solid support is silica.

60. The catalyst composition according to claim 50, wherein the solid support is silica.

INTERNATIONAL SEARCH REPORT

Int'l. Application No
PCT/US 00/03607

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F10/02 C08F4/70

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 48735 A (EXXON CHEMICAL PATENTS INC) 24 December 1997 (1997-12-24) cited in the application page 7, line 13 - line 16 page 27, line 10 -page 28, line 16; tables 1,2 page 41, line 10 -page 42, line 18; tables 13,14 ---	1-60
A	WO 98 40374 A (EASTMAN CHEM CO) 17 September 1998 (1998-09-17) cited in the application examples 36-91 ---	1-60
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 June 2000	11/07/2000
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel: (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016	Authorized officer Parry, J

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/03607

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SCHWARTZ, JEFFREY ET AL: "Nickel-catalyzed conjugate addition of alkenylzirconium species to. α ., β .-unsaturated ketones" J. AM. CHEM. SOC. (1980), 102(4), 1333-40 , XP000914840 page 1338; example 3B ---	1-60
P, X	MECKING ET AL: "Reactor blending with early/ late transition metal catalyst combinations in ethylene polymerization" MACROMOLECULAR: RAPID COMMUNICATIONS, DE, WILEY VCH, WEINHEIM, vol. 20, no. 3, 1 March 1999 (1999-03-01), pages 139-143, XP002106034 ISSN: 1022-1336 table 1 ---	1-60
P, X	WO 99 50318 A (E.I. DU PONT DE NEMOURS AND CO., USA) 7 October 1999 (1999-10-07) cited in the application examples 1-77; tables 1-10 -----	1-60

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PCT/US 00/03607

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		CN 1226257	A	18-08-1999
		EP 0906343	A	07-04-1999
		HU 9903930	A	28-03-2000
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		EP 0975682	A	02-02-2000
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